CHEMICAL REVIEWS

REVIEW

pubs.acs.org/CR

Organic Reactions Catalyzed by Rhenium Carbonyl Complexes

Yoichiro Kuninobu* and Kazuhiko Takai*

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Kita-ku, Okayama 700-8530, Japan

CONTENTS

1. INTRODUCTION

In the periodic table, rhenium is a group 7, sixth-row transition metal and is in the same group with manganese, technetium, and bohrium. Historically, rhenium was discovered as the last natural stable element. In 1908, Ogawa found a new element that he called nipponium and incorrectly reported as the 43rd element (the 43rd element is the artificial element technetium). It is believed today that the element he discovered was in fact element 75, or rhenium. It was not until 1925, however, that rhenium was officially discovered by Noddack, Tacke, and Berg. Rhenium is generally used as a catalyst for purification of petroleum, super heat-resistant alloys, and filaments. Since rhenium is quite rare and is available only in minor quantities, the price of rhenium metal is relatively high; it is cheaper, however, than palladium, rhodium, ruthenium, gold, and platinum, which play central roles in catalytic reactions.

There have been many reports on the synthesis of rhenium complexes.[1] Compared to other transition metal complexes, however, rhenium complexes have not been popular as catalysts for organic synthesis except in a few cases such as catalytic reactions with rhenium−oxo complexes or $MeReO_3$.[2] Therefore, the reactivity of rhenium complexes has not been explored as extensively as that of other transition metal complexes.[2,3]

Rhenium carbonyl complexes account for a significant portion of known rhenium complexes. Several, such as $Re_2(CO)_{10}$, $ReCl(CO)_5$, $ReBr(CO)_5$, $[ReBr(CO)_3(thf)]_2$, $CpRe(CO)_3$, and $Cp^*Re(CO)_3$ ($Cp^* = C_5Me_5$), are commercially available. In addition, many examples of rhenium carbonyl complexes have been reported in the literature. For example, phosphine complexes $Re_2(CO)_{(8-n)}(PR_3)_n$ (n = 1, 2),[4] nitrile complexes $Re_2(CO)_9(NCR)$,[5] isonitrile complexes $Re_2(CO)_{(8-n)}(CNR)_n$ (n = 1 to 4),[6] hydride complexes $Re_lH_m(CO)_n$,[7] and bipyridyl complexes $ReX(CO)_3(bpy)$ (X = Cl, Br, I, etc; bpy = bipyridyl)[8] are known.

Rhenium carbonyl complexes have four notable features. The first is their hard Lewis acidity. Oxygen, nitrogen, and halogen atoms coordinate to the rhenium center, generating cationic species or intermediates with large $\delta+$ values. Compared to popular hard Lewis acids, such as $AlCl_3$, the Lewis acidity of rhenium carbonyl complexes is moderate, and thus relatively stable carbocations (i.e., propargylic and benzylic carbocations and oxonium ions) can be generated by elimination of an alkoxy (or hydroxyl) group or halides. Further reactions with nucleophiles, such as Friedel−Crafts and Hosomi−Sakurai reactions, occur. It is necessary to note that, in contrast to $AlCl_3$, the Lewis acidity does not drop substantially in the presence of a small amount of water.

The second feature of rhenium carbonyl complexes is their soft Lewis acidity for activation of unsaturated hydrocarbons such as alkynes, allenes, and alkenes. Similar to gold or platinum halides, unsaturated hydrocarbons coordinate to rhenium carbonyl complexes, and due to the electron deficiency of the coordinated hydrocarbons, carbon, nitrogen, and oxygen nucleophiles can attack them. In some cases, rhenium−alkylidene

Special Issue: 2011 Frontiers in Transition Metal Catalyzed Reactions

Received: July 28, 2010
Published: November 23, 2010

ACS Publications © 2010 American Chemical Society

intermediates can be generated by successive reactions, and these intermediates then promote further reactions, such as cyclopropanation.

The third feature of rhenium carbonyl complexes is their ability to activate C(sp^2)−H and C(sp^3)−H bonds, allowing for introduction of several functional groups or substituents directly into C−H bonds. The first coordinatively unsaturated rhenium carbonyl complex effective for catalytic C−H transformations was generated via photoirradiation of Cp*Re(CO)$_3$ by Chen and Hartwig in 1997, and catalytic borylation at the terminal position of alkanes was realized.[9] In 2005, Kuninobu, Kawata, and Takai discovered that catalytic directed C−H activation at the *ortho*-position of aromatic imines occurs with ReBr(CO)$_5$ and related carbonyl complexes in toluene under heating conditions.[10] Since then, reactions initiated by rhenium-catalyzed C−H activation have been extensively studied. In contrast to ruthenium- and rhodium-catalyzed C−H activation, insertion of unsaturated molecules occurs between the rhenium−carbon bond and not the rhenium−hydrogen bond. In addition, the carbon connected to rhenium shows nucleophilicity due to the relatively small electronegativity of rhenium compared to ruthenium or rhodium. Therefore, the insertion of polar unsaturated molecules occurs, and cyclic compounds such as indenes and isobenzofurans are produced (vide infra), a reaction that cannot be achieved with ruthenium or rhodium catalysts.

Additionally, low-valent rhenium carbonyl complexes promote oxidative cyclization. Although the primary intermediate has not been isolated, [2 + 2]-cycloaddition products between norbornenes and alkynes derived by successive reductive elimination are obtained. When β-keto esters are used instead of norbornenes, cyclobutene intermediates having a β-hydroxy ester moiety can be generated. Because of the ring strain of the cyclobutene skeleton, C−C bond cleavage occurs via a retro-aldol reaction.

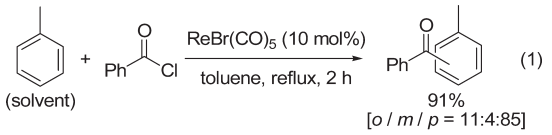
The above features enable rhenium carbonyl complexes to promote interesting catalytic transformations. Many types of reactions, such as the formation of carbon−carbon, carbon−silicon, carbon−nitrogen, carbon−oxygen, carbon−sulfur, and carbon−selenium bonds, reduction, and polymerization are possible. The details of such rhenium carbonyl complex-catalyzed synthetic organic reactions and, for some cases, their mechanisms are described below.

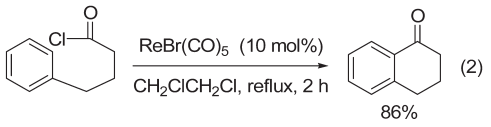
2. C−C BOND FORMATION

2.1. Nucleophilic Addition and Substitution

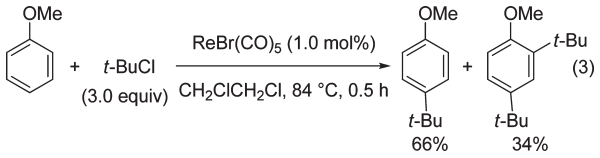
2.1.1. Friedel−Crafts Reactions. The Friedel−Crafts reaction is one of the most fundamental and useful transformations in synthetic chemistry. There are mainly two types of such reactions: Friedel−Crafts acylation and Friedel−Crafts alkylation. These reactions are usually promoted by strong Lewis or Brønsted acids. The following several examples of Friedel−Crafts acylation and alkylation show that rhenium(I)−carbonyl complexes also have hard Lewis acidity.

Kusama and Narasaka reported that a rhenium complex, ReBr(CO)$_5$, catalytically promotes Friedel−Crafts acylation (eq 1).[11] Conventional Friedel−Crafts acylations usually require at least an equimolar amount of Lewis acid. From this standpoint, it is noteworthy that the rhenium-catalyzed reaction proceeds catalytically; however, the product is obtained as a mixture of regioisomers. Although the acylations of toluene, *m*-xylene, and anisole proceed smoothly, the yield of the acylation of benzene is low. Intramolecular acylation of aromatic rings does occur regioselectively, though, affording indanone and tetralone (eq 2).[11]

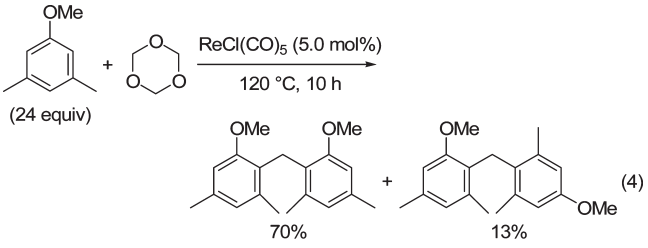




Rhenium-catalyzed Friedel−Crafts alkylation of arenes has been reported by Nishiyama, Kakushou, and Sonoda (eq 3).[12] Conventional Friedel−Crafts alkylations generally proceed catalytically, but the reactions are sometimes carried out under strongly acidic conditions. In contrast, the rhenium-catalyzed Friedel−Crafts alkylation proceeds under weakly acidic conditions. The intermolecular reaction generates a mixture of mono- and dialkylated products, whereas the intramolecular alkylation gives indane derivatives selectively.



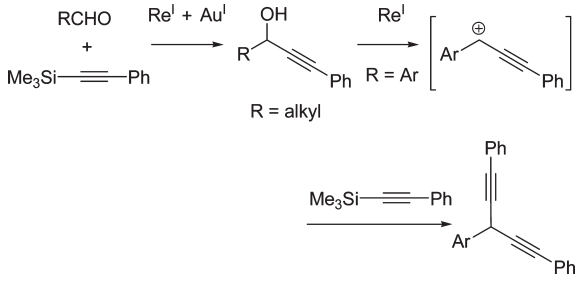
By using the Lewis acidity of rhenium(I) complexes, diarylmethanes have been synthesized from 2 equiv of aromatic compounds and 1,3,5-trioxane (or aqueous formaldehyde) (eq 4).[13] Aromatic compounds with an electron-donating group(s) are tolerated in the reaction, and a mixture of regioisomers is formed. This reaction proceeds via the formation of benzylic alcohols from aromatic compounds and 1,3,5-trioxane (or formaldehyde). The corresponding benzyl cations generated from the benzylic alcohols and the rhenium catalyst react with another aromatic compound. In these steps, ReCl(CO)$_5$ functions as a Lewis acid even in the presence of a small amount of water.



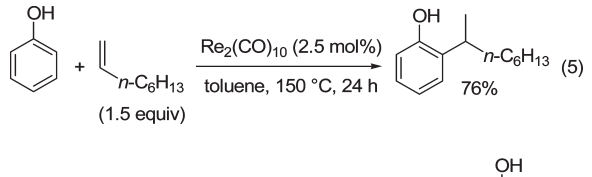
Another reaction that produces Friedel−Crafts type adducts has been reported for the rhenium complex Re$_2$(CO)$_{10}$. Combining phenol and a terminal olefin in the presence of a catalytic amount of Re$_2$(CO)$_{10}$ leads to monoalkylation only at the position *ortho* to the hydroxyl group (eq 5).[14] It is usually difficult to perform monoalkylation regioselectively using conventional Friedel−Crafts conditions. Judging from the regioselectivity of the monoalkylation and given the fact that monoalkylation occurs only when the terminal olefin is used as a solvent (excess amount), it is likely that this reaction does not proceed via a Friedel−Crafts alkylation mechanism. On the other hand, when 2-alkyl substituted olefins and conjugated

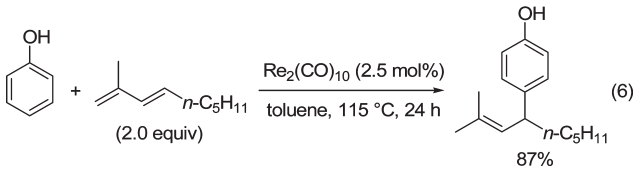
dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

Scheme 1. Proposed Mechanism for the Formation of Dialkynylmethanes



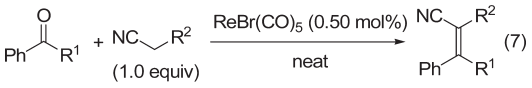
dienes are used, alkylation proceeds regioselectively at the *para*-position (eq 6).[14]





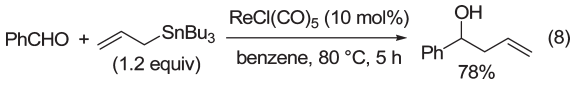
2.1.2. Nucleophilic Addition to Carbonyl and Related Compounds. Carbon−carbon bond-forming reactions by nucleophilic addition of carbon nucleophiles to carbonyl compounds are some of the most effective synthetic methods. Rhenium(I) carbonyl complexes catalyze Knoevenagel condensations, allylation of aldehydes, Mukaiyama aldol reactions, and diethynylation of aldehydes. In these transformations, the catalysts act as hard Lewis acids.

Komiya and co-workers reported that *N*-bonded enolate rhenium(I) complexes promote the Knoevenagel condensation between aldehydes and active methylene compounds.[15] A similar reaction proceeds when the rhenium complex is changed to $ReBr(CO)_5$ (eq 7).[16] Notably, this reaction takes place in the absence of solvent. In the case of aldehydes and unsymmetrical active methylene compounds, the stereoselectivities of the products are quite high; however, the stereoselectivity decreases when unsymmetrical ketones are employed as substrates.

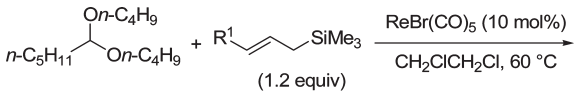


R^1	R^2	conditions	yield / %
H	CN	110 °C, 1.5 h	90
H	CO_2Et	110 °C, 2 h	88
Me	CO_2Et	130 °C, 70 h	45 [*E*/*Z* = 3/2]

Rhenium-catalyzed allylation of aldehydes with allyltributylstannane has been reported by Nishiyama, Kakushou, and Sonoda (eq 8).[17] In this reaction, homoallylic alcohols are obtained in moderate to good yields using aromatic or aliphatic aldehydes. In contrast to $ReCl(CO)_5$, the rhenium carbonyl complexes $Re_2(CO)_{10}$ and $CpRe(CO)_3$ did not show this catalytic activity.

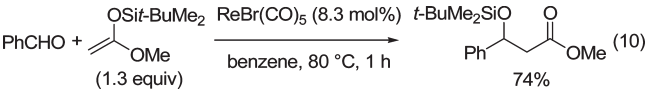


$ReBr(CO)_5$ also catalyzes allylation of acetals with allyltrimethylsilane (eq 9).[18] In this reaction, only monoallylated products are produced. When crotyltrimethylsilane is employed, a mixture of the *anti*- and *syn*-forms of the γ-adducts and the *E*- and *Z*-forms of the α-adducts are obtained.

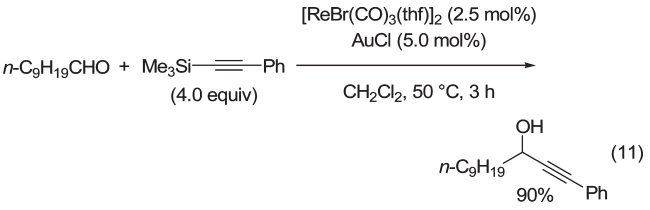


R^1		product
H	5 h	On-C4H9, n-C5H11 (92%)
Me	24 h	On-C4H9, n-C5H11 (26%, [*anti*/*syn* = 56/44]) + On-C4H9, n-C5H11 (6%, [*E*/*Z* = 72/28])

This rhenium complex also catalyzes the Mukaiyama aldol reaction between carbonyl compounds and ketene silyl acetals (eq 10).[19] In this reaction, not only aldehydes but also ketones can be used as substrates. Ketene silyl acetals with a methyl group at the β-position provide a mixture of *anti*- and *syn*-products.



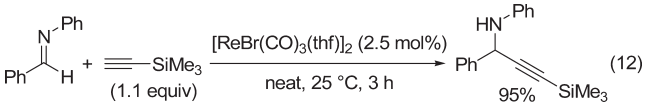
When silylacetylenes serve as the nucleophile, use of a rhenium(I) carbonyl complex alone is not effective; addition of AuCl as a cocatalyst, however, leads to formation of propargylic alcohols via addition of the silylacetylene to the aldehyde (eq 11).[20] Interestingly, both the rhenium and gold catalysts are indispensable for promoting the reaction. When 2 equiv of silylacetylenes are employed, the synthesis of diethynylmethanes from aldehydes is achieved.[20] This reaction proceeds by rhenium- and gold-catalyzed formation of propargylic alcohols from aldehydes and silylacetylenes, followed by rhenium-catalyzed alkynylation of the formed propargylic alcohols with the second silylacetylene (Scheme 1).



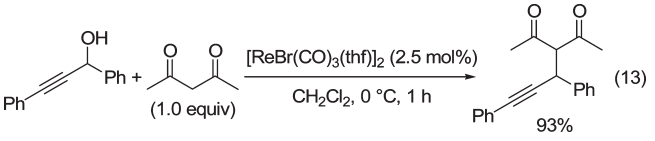
Addition of terminal alkynes to imines is a useful method for the synthesis of propargyl amines. $[ReBr(CO)_3(thf)]_2$ promotes the addition of trimethylsilylacetylene to aldimines (eq 12).[21] In this reaction, the silyl group connected to the alkyne moiety is

dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

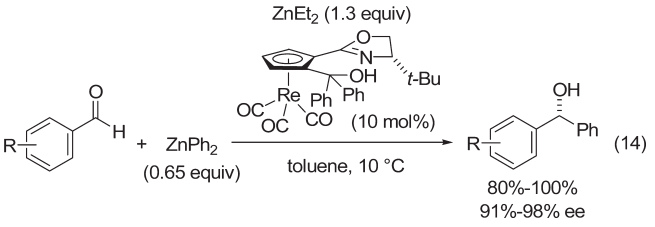
indispensable for the reaction and remains unchanged. This catalytic activity is similar to that of an iridium complex reported by Fischer and Carreira.[22]



Nucleophilic substitution of 2-propynyl alcohols with active methylene compounds has also been reported (eq 13).[23] In this reaction, a new carbon−carbon single bond is constructed. By using carbon, oxygen, and sulfur nucleophiles, carbon−carbon, carbon−oxygen, and carbon−sulfur bonds can be generated. Interestingly, the rhenium catalyst remains active even in the presence of a small amount of water.

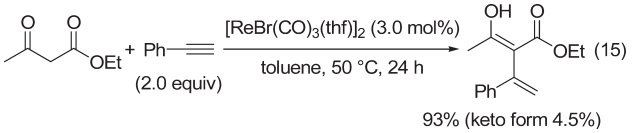


Highly enantioselective addition of diphenylzinc to aldehydes has been achieved by Bolm and co-workers (eq 14).[24] The authors synthesized a planar chiral rhenium complex and applied the complex to the addition reaction as a planar chiral ligand. Compared to its analogous ferrocene derivative, the rhenium complex showed higher enantioselectivities.

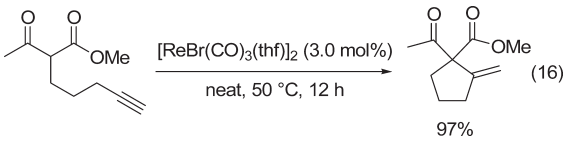


2.1.3. Nucleophilic Addition to C−C Double and Triple Bonds. Nucleophilic addition of carbon nucleophiles to unactivated (nonpolar) carbon−carbon double or triple bonds is usually difficult. By activating carbon−carbon double or triple bonds with transition metal catalysts, such transformations have recently been realized. Coordination of the carbon−carbon double or triple bonds to soft Lewis acids is important for promoting these reactions. As described in sections 2.1.1 and 2.1.2, rhenium(I) carbonyl complexes act as hard Lewis acids. We see here that rhenium complexes also have soft Lewis acidity.

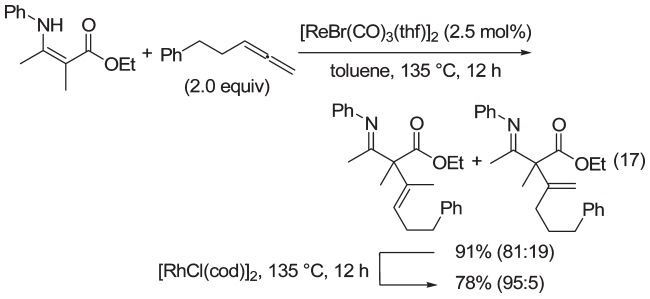
Nakamura and co-workers reported indium-catalyzed addition of active methylene compounds to alkynes.[25] A similar reaction also occurs when the rhenium complex $[ReBr(CO)_3(thf)]_2$ is used as the catalyst (eq 15).[26,27] This reaction proceeds even with unactivated alkynes, although only terminal alkynes can be used.



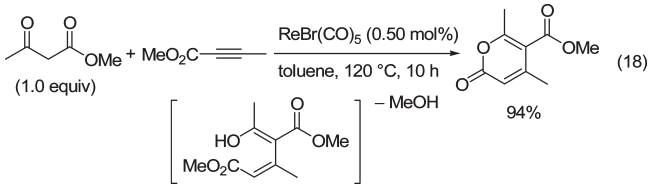
An intramolecular version of this transformation (Conia-ene type reaction) that yields methylenecycloalkanes has also been investigated (eq 16).[26,27] Similar reactions are also promoted by gold,[28] nickel/ytterbium,[29] copper/silver,[30] and zinc[31] catalysts.



Nucleophilic addition of active methylene compounds also proceeds using allenes as electrophiles. Reaction of β-enamino esters and unactivated allenes using the rhenium complex $[ReBr(CO)_3(thf)]_2$ proceeds at the central position of the allene moiety, and the products are generated as a mixture of olefinic isomers (eq 17).[32] The regioselectivity is improved by further isomerization of the olefin moieties with the rhodium complex $[RhCl(cod)]_2$ as a catalyst.

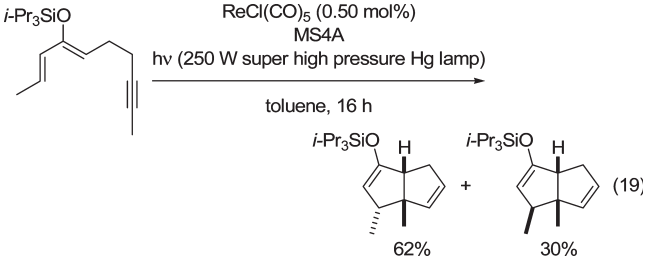


Nucleophilic addition of active methylene compounds to activated alkynes (polar alkynes) and its application to the synthesis of 2*H*-pyran-2-ones has been reported by Zhao and Hua. (eq 18).[33] This reaction proceeds via addition of β-keto esters to electron-deficient alkynes followed by intramolecular nucleophilic cyclization and elimination of methanol.



2.2. Annulations

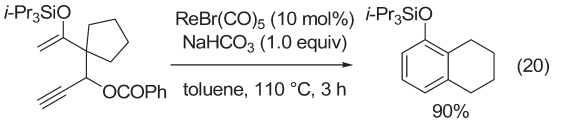
2.2.1. Annulation via Alkylidene Intermediates. Kusama, Iwasawa, and co-workers reported that the rhenium complex $ReCl(CO)_5$ catalyzes tandem cyclization of ω,ω-acetylenic dienol silyl ethers (eq 19).[34] The authors had already reported that the tungsten complex $W(CO)_5(thf)$ can activate terminal alkynes toward the catalytic intramolecular nucleophilic attack of enol silyl ethers to give carbocycles.[35] In the reaction shown in eq 19, the rhenium complex activates the internal alkyne moiety and realizes geminal carbofunctionalization of alkynes. This reaction also proceeds with $W(CO)_6$, $PtCl_2$, or $AuBr_3$ as the catalyst.



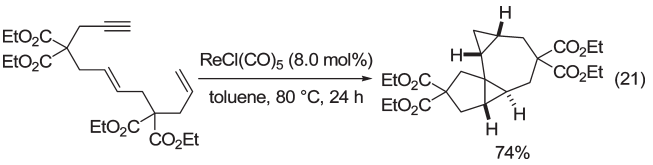
dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

The mechanism of this reaction is as follows: (1) coordination of the alkyne moiety of an acetylenic dienol silyl ether to a rhenium center; (2) nucleophilic attack of the dienol silyl ether moiety to the activated alkyne moiety to generate a zwitterionic intermediate; (3) intramolecular attack of the alkenyl rhenium moiety to the α,β-unsaturated silyloxonium group, generating a bicyclic carbene intermediate; and (4) 1,2-hydrogen migration to produce a bicyclo[3.3.0]octane derivative (Scheme 2).

By changing the substrates to silyl enol ethers bearing a propargyl carboxylate moiety, substituted phenols were obtained (eq 20).[36] The proposed mechanism for the formation of phenol derivatives is shown in Scheme 3: (1) intramolecular nucleophilic addition of the silyl enol moiety to the activated alkyne moiety to give a zwitterionic six-membered cyclic intermediate; (2) formation of a silyl dienol ether intermediate by deprotonation; (3) elimination of a benzoate to provide a cationic pentadienyl intermediate; (4) migration of an alkyl group; and (5) protonation of the C−Re bond to produce a phenol derivative.

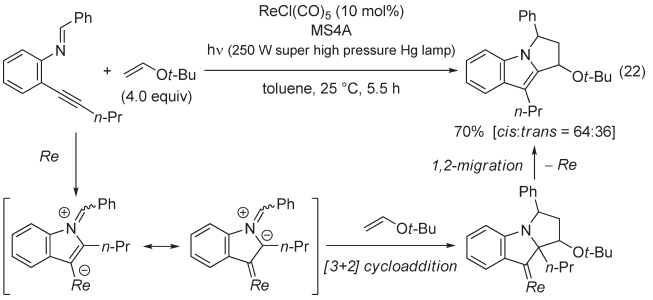


The construction of polycyclic ring skeletons by cycloisomerization of ene−ene−ynes with a catalytic amount of transition metal complexes has been reported by Chatani, Murai, and co-workers. (eq 21).[37] In this reaction, $[RuCl_2(CO)_3]_2$, $[Rh(OCOCF_3)_2]_2$, and $PtCl_2$ are effective for promoting the transformation. Other transition metal complexes including $ReCl(CO)_5$ also catalyze the reaction, which proceeds via the formation of a rhenium carbenoid intermediate.

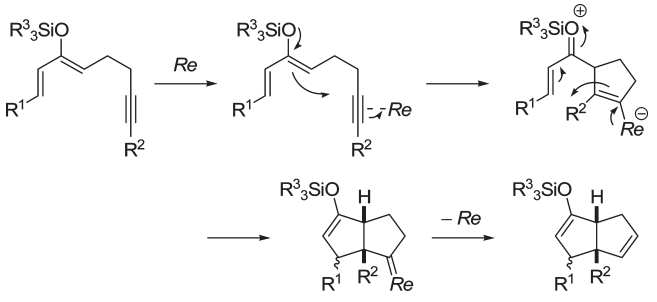


Two possible pathways have been proposed for the formation of intermediate **A** (Scheme 4). The first possibility involves formation of a rhenacyclopentene intermediate (1-a) followed by migration of the rhenacyclopentene intermediate to the rhenium−carbene intermediate **A** (2-a). An alternative pathway begins with formation of a zwitterionic rhenium intermediate (1-b) that undergoes bond migration to produce a rhenium carbene intermediate with a carbene moiety (2-b), with intramolecular cyclization between the carbene and olefin groups (3-b) producing rhenium−carbene intermediate **A**. In the final steps in the mechanism, intermediate **A** undergoes [2 + 2]-cycloaddition between the rhenium−carbene and olefin moieties (4) followed by reductive elimination (5).

Kusama, Iwasawa, and co-workers succeeded in developing [3 + 2]-cycloadditions of metal-containing azomethine ylides catalyzed by $PtCl_2$ or $AuBr_3$ to give mitosene skeletons (eq 22).[38] Similar catalytic activity is observed with $ReCl(CO)_5$ when the reaction mixture is irradiated with a super high pressure mercury lamp. This reaction proceeds via the formation of a transition metal-containing azomethine ylide and a carbene complex.

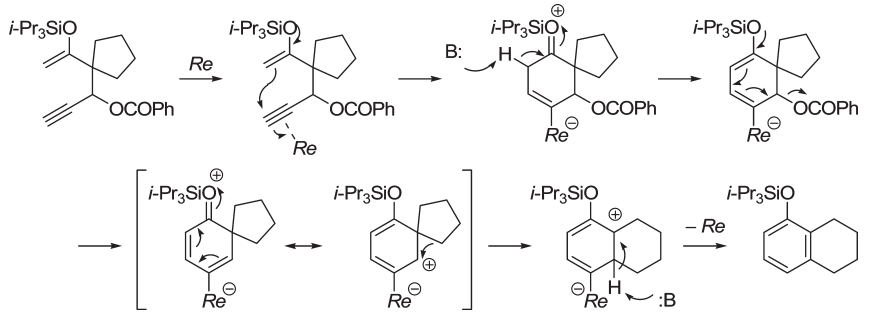


Scheme 2. Proposed Mechanism for the Formation of Bicyclo[3.3.0]octane Derivatives



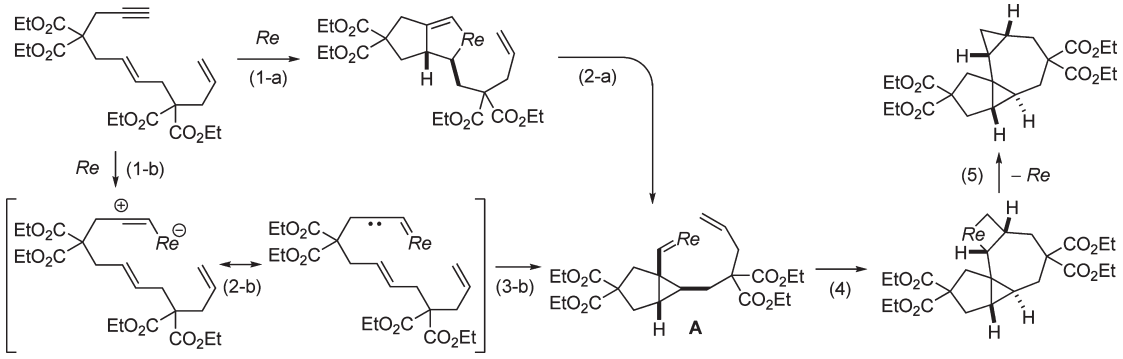
2.2.2. [2 + 2]-, [3 + 2]-, and [2 + 2 + 2]-Cycloaddition Reactions. [2 + 2]-Cycloaddition of norbornenes with internal and terminal alkynes proceeds with $[ReBr(CO)_3(thf)]_2$ as the catalyst (eq 23).[39] In this reaction, the yields of the cyclobutene derivatives are improved by addition of a catalytic amount of an isocyanide. The reaction proceeds via oxidative cyclization

Scheme 3. Proposed Mechanism for the Formation of Phenol Derivatives

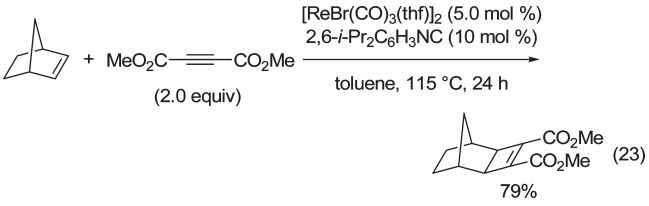


dx.doi.org/10.1021/cr100241u |Chem. Rev. 2011, 111, 1938–1953

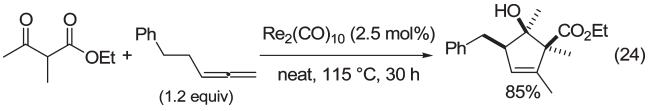
Scheme 4. Proposed Mechanism for the Cycloisomerization of Ene−Ene−Ynes



between the rhenium catalyst, norbornene, and alkyne, with successive reductive elimination.



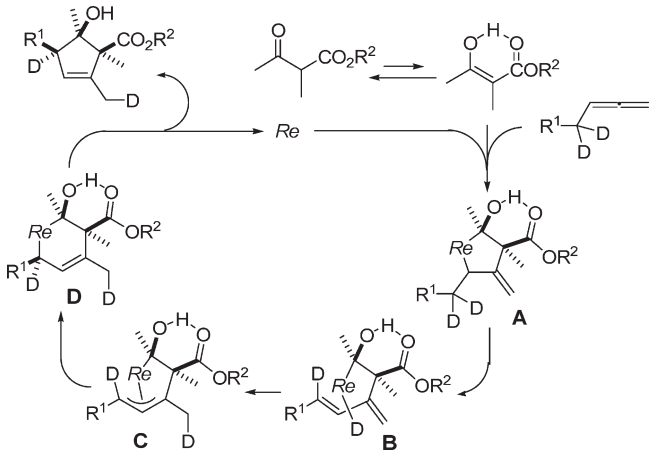
Cycloaddition reactions are one of the most efficient methods to synthesize cyclic compounds, and thus many methods have been developed to construct cyclic skeletons. It is usually difficult, however, to achieve the formation of cyclic compounds regio- and stereoselectively. Yudha, Kuninobu, and Takai succeeded in the regio- and stereoselective synthesis of cyclopentene derivatives from β-keto esters and allenes using $Re_2(CO)_{10}$ as a catalyst (eq 24).[40] In this reaction, the stereochemistry of three carbon centers is defined completely.



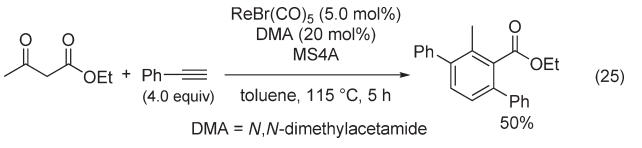
The proposed mechanism of this reaction, based on a deuterium-labeled experiment, is as follows (Scheme 5): (1) oxidative cycloaddition of the enol form of the β-keto ester, the allene, and the rhenium catalyst to give rhenacyclopentane intermediate **A**; (2) β-hydride elimination to form diene intermediate **B**; (3) insertion of the olefin moiety of intermediate **B** into a Re−H bond to produce π-allyl rhenium intermediate **C**; and (4) formation of a rhenacyclohexene intermediate **D** followed by reductive elimination to give the cyclopentene derivative regio- and stereoselectively.

[2 + 2 + 2]-Cycloaddition reactions, such as cyclotrimerization of alkynes, are powerful methods for synthesizing substituted aromatic compounds. It is generally difficult, however, to control pair- and regioselectivity. Regioselective [2 + 2 + 2]-cycloaddition reactions between 1,3-dicarbonyl compounds and terminal alkynes with catalytic amounts of the rhenium complex $ReBr(CO)_5$ and *N*,*N*-dimethylacetamide have been achieved, however (eq 25).[41] In this reaction, two aryl groups of the product orient in the *para*-position with respect to each other. The manganese complex $MnBr(CO)_5$ has independently been

Scheme 5. Proposed Mechanism for the Formation of Stereodefined Cyclopentene Derivatives



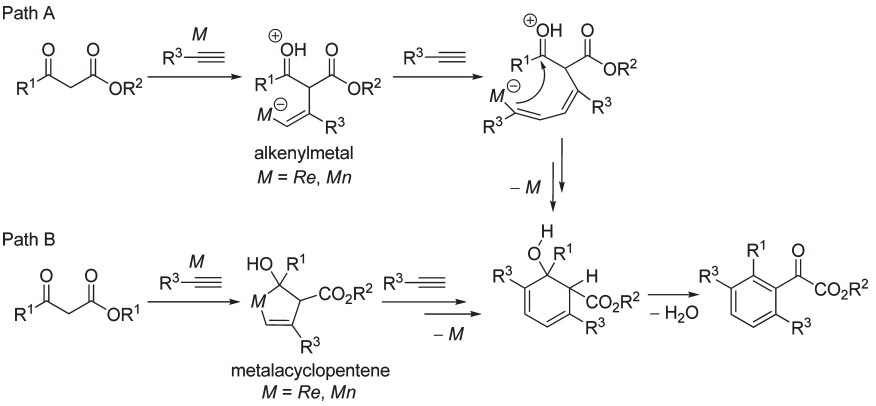
shown to exhibit higher catalytic activity in this transformation by the same research group[27,41] and by Tsuji and Nakamura's group.[42] To explain the regioselective formation of the tetrasubstituted aromatic compounds, there are two possible reaction pathways (Scheme 6). The first possibility is the formation of an alkenyl−manganese intermediate via the stepwise insertion of two alkynes in the opposite orientation to each other (Scheme 6, path A). Very recently, Nakamura, Tsuji, and co-workers reported on the mechanistic study of the [2 + 2 + 2]-cycloaddition.[43] They concluded that the reaction proceeds via this route. The second possibility is that the reaction occurs via the formation of a metalacyclopentene intermediate that is produced from a 1,3-dicarbonyl compound and an alkyne (Scheme 6, path B).[27]



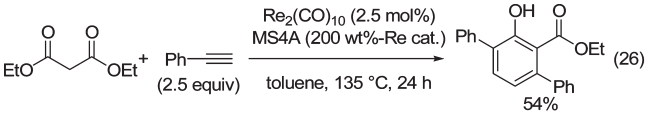
When malonates without a substituent at the active methylene moiety are treated with terminal alkynes, salicylates are obtained regioselectively (eq 26).[44] In contrast, when malonates bearing a substituent at the active methylene moiety are used, cyclic β-keto esters are generated regioselectively. Treatment of the formed

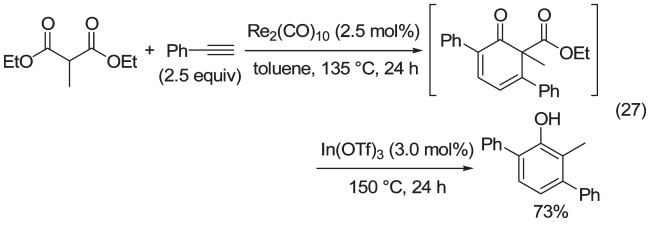
dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

Scheme 6. Proposed Mechanism for the Formation of Tetrasubstituted Aromatic Compounds

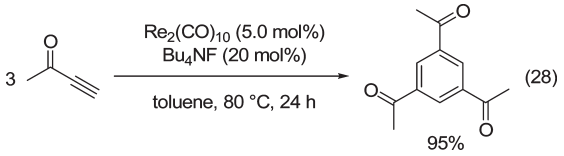


cyclic β-keto esters with $In(OTf)_3$ yields phenol derivatives via decarbonylation (eq 27).[44]



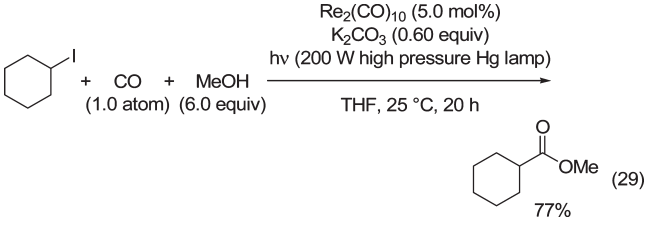


Regioselective cyclotrimerization of alkynes is difficult, as mentioned previously. Notably, however, the rhenium complex $Re_2(CO)_{10}$ catalyzes the regioselective cyclotrimerization of terminal alkynes containing an electron-withdrawing substituent (eq 28).[45] In this reaction, only 1,3,5-trisubstituted aromatic compounds are obtained.

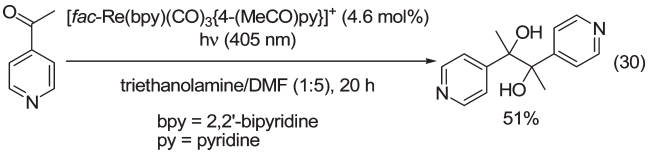


2.3. Coupling Reactions

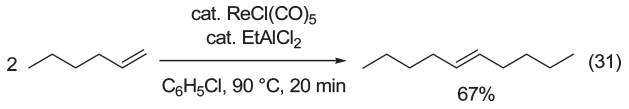
Three-component coupling reactions are efficient transformations for constructing complex organic molecules. Watanabe and co-workers reported the coupling reaction between alkyl iodides, carbon monoxide, and alcohols to give the corresponding esters in the presence of a catalytic amount of rhenium complex $Re_2(CO)_{10}$ under UV-irradiation conditions (eq 29).[46] This reaction also proceeds using other transition metal carbonyl complexes such as $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $Pt(CO)_2(PPh_3)_2$.



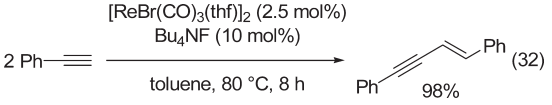
Photochemical reductive coupling of acetylpyridine to the corresponding pinacol catalyzed by rhenium complex $[fac\text{-}Re(bpy)(CO)_3\{4\text{-}(MeCO)py\}]^+$ (bpy = 2,2-bipyridine; py = pyridine) has been reported by Hori, Ishitani, and co-workers (eq 30).[47] The reaction was found to proceed not via simple photosensitization of $[fac\text{-}Re(bpy)(CO)_3\{4\text{-}(MeCO)py\}]^+$ for the electron transfer but rather via the reaction on the ligand of the rhenium complex. The pinacol complex $[fac\text{-}Re(bpy)(CO)_3\{py\text{-}CMe(OH)CMe(OH)\text{-}py\}]^+$ is proposed as a reaction intermediate.



Farona and Greenlee reported that a mixture of catalytic amounts of $ReX(CO)_5$ (X = Cl or Br) and $EtAlCl_2$ promoted olefin metathesis of terminal and internal olefins (eq 31).[48] This catalytic system was also found to show high stability and can be recycled for several days.



There have been many reports on dimerization of terminal alkynes; however, a mixture of (*E*)-1,4-disubstituted, (*Z*)-1,4-disubstituted, and 2,4-disubstituted enynes is usually formed.[49] By using $[ReBr(CO)_3(thf)]_2$ and tetrabutylammonium fluoride as catalysts, terminal aromatic alkynes are dimerized to produce only (*E*)-enynes (eq 32).[45] In this reaction, arylacetylenes gave (*E*)-enynes in excellent yields and enynes afforded trienynes in moderate yields. However, alkylacetylenes and silylacetylenes did not produce the desired products.



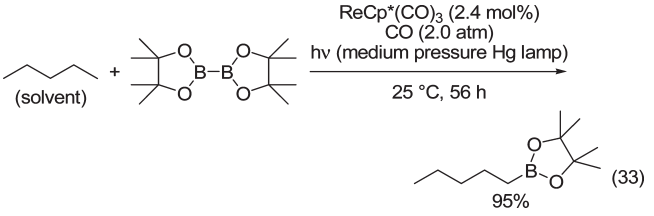
2.4. Reactions Based on C−H Bond Activation

Carbon−hydrogen (C−H) bonds are fundamental and ubiquitous bonds in organic molecules. Therefore, transformations

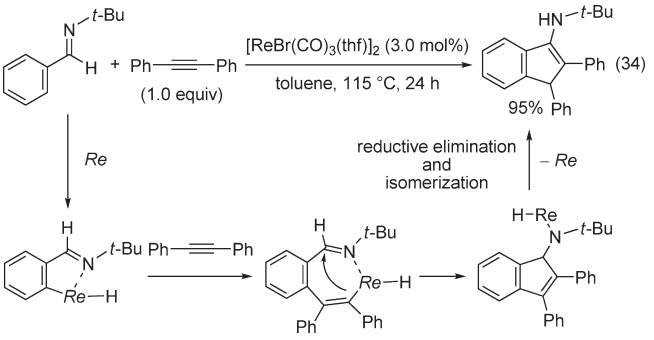
dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

starting from a C−H bond are direct and efficient methods for construction of more complex molecules. Selective transformations via C−H bond activation are usually difficult, however, because the bond energy of C−H bonds is high and there are many kinds of C−H bonds in a molecule. Despite these challenges, there have recently been many reports on C−H transformations.[50] In this section, we focus on reactions based on rhenium-catalyzed C−H activation.

In 1997, Waltz and Hartwig reported that monoboryl complexes of tungsten functionalize alkanes stoichiometrically.[51] Two years later, the same group showed that a rhenium(I) carbonyl complex can promote C(sp^3)−H functionalization catalytically. A rhenium complex, Cp*Re(CO)$_3$, catalyzed C(sp^3)−H borylation at the terminal position of alkanes under photochemical conditions (eq 33).[9] This reaction requires photoirradiation to generate a coordinatively unsaturated rhenium complex and proceeds with essentially perfect regioselectivity. Since then, this chemistry has been expanded to other transition-metal-catalyzed reactions.[52] Notably, reactions with ruthenium and rhodium catalysts require high temperatures (150 °C). In contrast, the rhenium-catalyzed borylation occurs even at 25 °C.



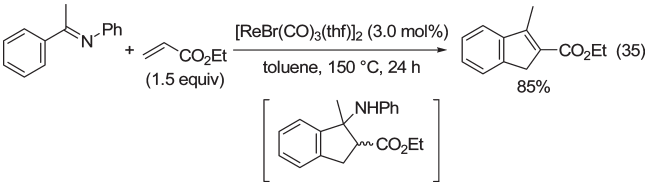
Rhenium(I) carbonyl complexes also catalyze C(sp^2)−H bond functionalization. In 2005, Kuninobu, Kawata, and Takai succeeded in synthesizing aminoindene derivatives from aromatic aldimines and alkynes using a rhenium complex [ReBr(CO)$_3$(thf)]$_2$ as the catalyst (eq 34).[10] The reaction does not occur with aromatic aldehydes. It proceeds via the following steps: (1) coordination of a nitrogen atom of the imine to the rhenium center; (2) C−H bond activation (formation of an *ortho*-metalated imine); (3) insertion of an alkyne into the rhenium−carbon bond of the aryl−rhenium intermediate; (4) intramolecular nucleophilic attack of the formed alkenylrhenium moiety on a carbon atom of the imine; and (5) reductive elimination and 1,3-rearrangement of the hydrogen atoms (or vice versa).



Before the report of this reaction, ruthenium and rhodium complexes were usually employed as catalysts for C(sp^2)−H functionalization; only products derived from insertion of unsaturated molecules into a C−H bond were obtained, however.[50] In contrast, [ReBr(CO)$_3$(thf)]$_2$ catalyzes intramolecular nucleophilic cyclization following C−H activation and insertion of the unsaturated molecules to produce indene derivatives. This result reveals several typical features of this rhenium-catalyzed reaction. First, insertion of unsaturated molecules occurs into the metal (rhenium)−carbon bond generated by C−H activation with the rhenium complex. This shows sharp contrast to reactions with ruthenium or rhodium complexes, where insertion of the unsaturated molecule occurs at the metal−hydrogen bond.[53] Second, the sp^2-carbon connected to rhenium generated in the insertion step has nucleophilicity for intramolecular cyclization because rhenium has a smaller electronegativity than ruthenium or rhodium, and thus the rhenium−carbon bond is more polarized than the ruthenium− or rhodium−carbon bonds. The formation of the indene skeleton suggests that the cyclization proceeds faster than reductive elimination, which would lead to a simple insertion product (Scheme 7).

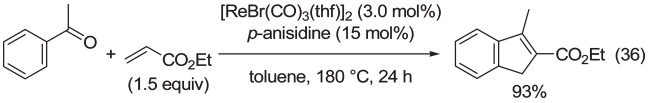
As shown in Scheme 7, an sp^2-carbon connected to the metal (rhenium), which is a potential nucleophilic site, also exists just after the C−H activation. When the rhenium complex [ReBr(CO)$_3$(thf)]$_2$ is used, insertion of polar unsaturated molecules such as α,β-unsaturated esters, aldehydes, and isocyanates occurs, and successive intramolecular nucleophilic cyclization proceeds to give the corresponding cyclic compounds.

By the reaction of aromatic ketimines with acrylates under rhenium catalysis, ([ReBr(CO)$_3$(thf)]$_2$), indene derivatives are formed after intramolecular cyclization and successive elimination of aniline (eq 35).[54]



As a result of detailed investigations, the reaction mechanism has been clarified as follows.[53] Activation of an *ortho*-C−H bond is accelerated by the coordination of a nitrogen atom of the ketimine to the rhenium center, generating an arylrhenium intermediate. After C−H bond activation, an α,β-unsaturated compound inserts into the Re−C bond of the arylrhenium intermediate. Intramolecular nucleophilic cyclization of the Re−C bond to the imine moiety followed by reductive elimination and the elimination of aniline affords the indene derivative. The elimination of aniline is accelerated by the rhenium catalyst.

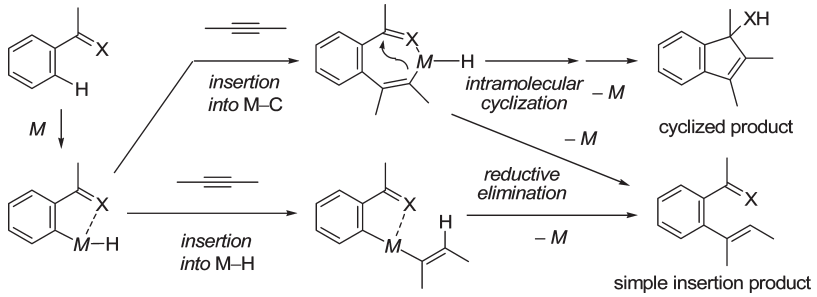
Because aromatic ketimines are synthesized from aromatic ketones and anilines via dehydration, and because the rhenium catalyst [ReBr(CO)$_3$(thf)]$_2$ shows a catalytic activity even in the presence of a small amount of water, the authors could apply the reaction in eq 35 to the synthesis of indenes using aromatic ketones and acrylates with aniline as a cocatalyst (eq 36).[54−56] In this reaction, the cycloaddition between aromatic ketones and acrylates proceeds with elimination of water.



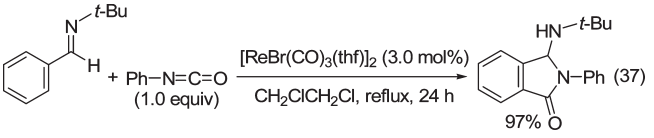
The rhenium complex [ReBr(CO)$_3$(thf)]$_2$ also catalyzes the insertion of polar unsaturated molecules such as isocyanates[57]

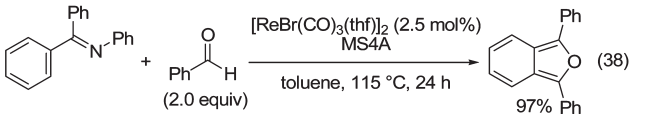
dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

Scheme 7. Insertion of an Alkyne into the Formed M−C or M−H Bond

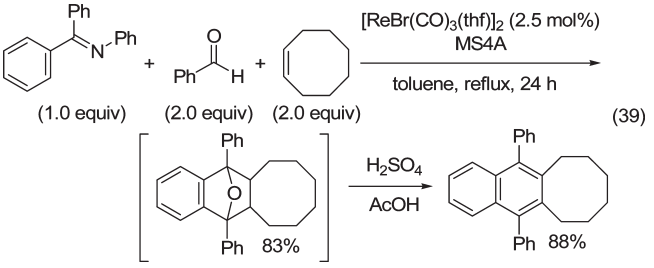


and aldehydes[58] into C−H bonds of aromatic compounds to produce phthalimidine and isobenzofuran derivatives (eqs 37 and 38). The nucleophilic reaction can be carried out intermolecularly. These results show sharp contrast to ruthenium and rhodium catalysts, for which the insertion of polar unsaturated molecules into a C−H bond has not been reported.

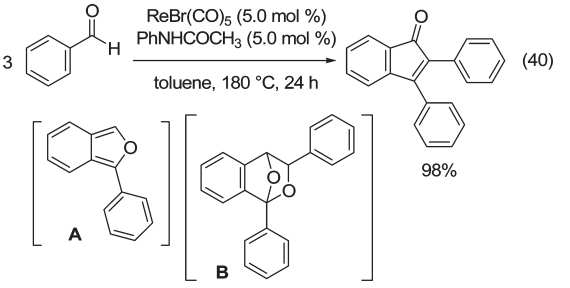


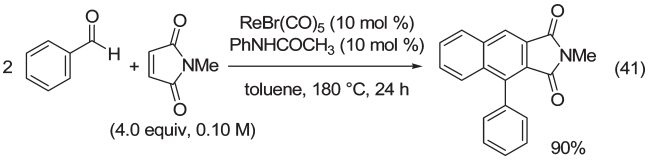


Because isobenzofuran derivatives have highly reactive diene moieties, these compounds act as good substrates for Diels−Alder reactions. The authors have carried out the reaction shown in eq 38 in the presence of an olefin (eq 39).[59] After treatment of the Diels−Alder adduct formed by the reaction of the isobenzofuran derivative and the alkene with acid, dehydration occurs to yield naphthalene derivatives.

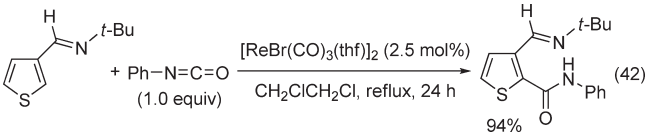


Dehydrative trimerization of aryl aldehydes takes place in the presence of catalytic amounts of $ReBr(CO)_5$ and *N*-phenylacetamide (eq 40).[60] Although the components of the formed indenone derivatives are the single aldehydes, this reaction is a new type of cyclotrimerization of aldehydes. The reaction proceeds via the following steps: (1) formation of an isobenzofuran derivative by the insertion of an aldehyde into the C−H bond of another aldehyde derivative (C−H bond activation) and successive intramolecular nucleophilic cyclization; (2) nucleophilic addition of the formed isobenzofuran derivative **A** to the third aldehyde and cyclization leading to **B**; (3) isomerization; and (4) intramolecular aldol condensation. To elucidate the reaction mechanism, the isobenzofuran intermediate **A** was trapped by dienophiles such as *N*-methylmaleimide (eq 41).

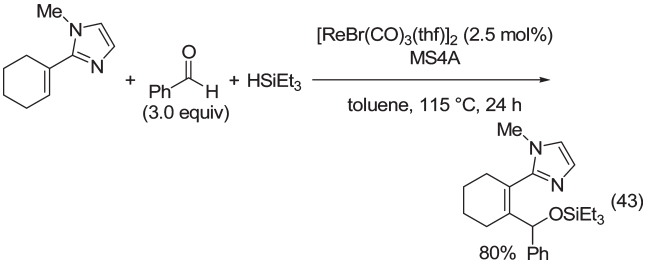




The rhenium complex $[ReBr(CO)_3(thf)]_2$ also activates heteroaromatic C−H bonds. Notably, the insertion of isocyanates, alkynes, and acrylates into C−H bonds of heteroaromatic compounds occurs regioselectively (eq 42).[61]



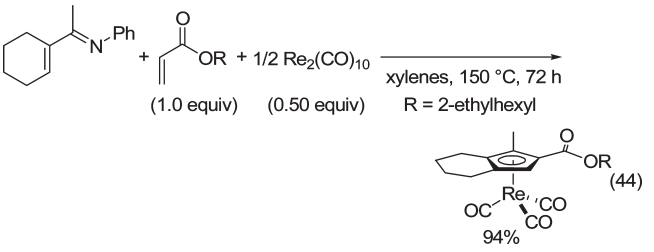
Rhenium complexes also promote olefinic C−H bond functionalization (eq 43).[62] When $[ReBr(CO)_3(thf)]_2$ is employed as a catalyst, insertion of nonpolar and polar unsaturated molecules into an olefinic C−H bond occurs.



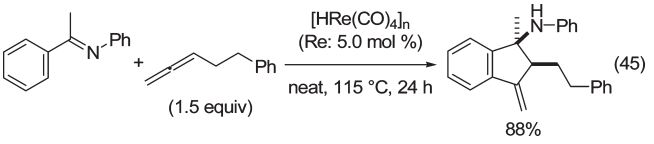
This reaction has been applied to the synthesis of cyclopentadienyl−rhenium (Cp−Re) complexes. When 0.50 equiv of

dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

$Re_2(CO)_{10}$ is used, Cp−Re complexes are produced from α,β-unsaturated ketimines and acrylates or vinylketones (eq 44).[63] The rhenium catalyst promotes C−H bond activation followed by insertion of an acrylate, intramolecular nucleophilic cyclization, and finally the elimination of aniline to give the cyclopentadiene derivative, which then complexes to the metal. In this reaction, the rhenium complex acts as a catalyst for C−H functionalization and also a component of the product Cp−Re complexes.



Diastereoselective synthesis of aminoindane derivatives has been achieved using $[HRe(CO)_4]_n$ as a catalyst (eq 45).[64] In this reaction, a quaternary carbon center was constructed and the relative stereochemistries of the two stereogenic centers of the aminoindanes were defined completely. There has been only one report on transition-metal-catalyzed insertion of an allene into a C−H bond of aromatic compounds.[65] In this reaction, the terminal carbon−carbon double bond of an allene inserts into an aromatic C−H bond. However, in eq 45, the insertion occurs at the internal carbon−carbon double bond of an allene.

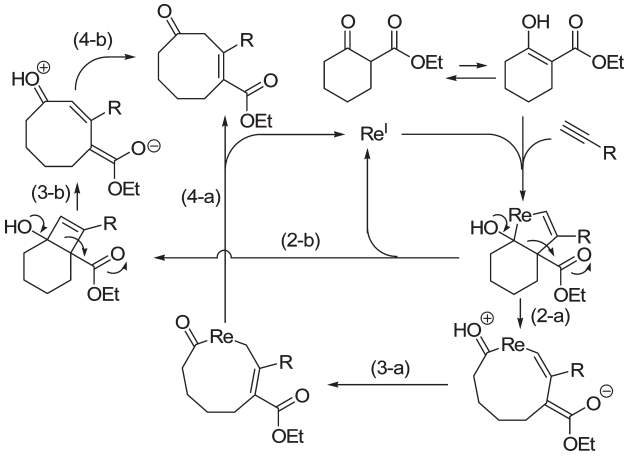


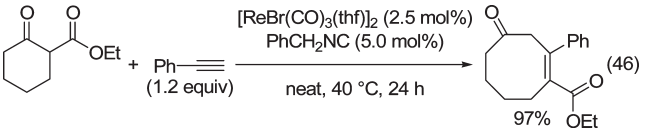
2.5. Reactions Initiated by C−C Bond Cleavage

Carbon−carbon (C−C) single bonds are fundamental structural bonds in organic molecules. It is usually hard to cleave C−C single bonds because their bond energy is quite high, and thus other bonds are cleaved preferentially. Development of insertion reactions at C−C bond is very important, however, because such transformations are direct and efficient methods for constructing new carbon skeletons.

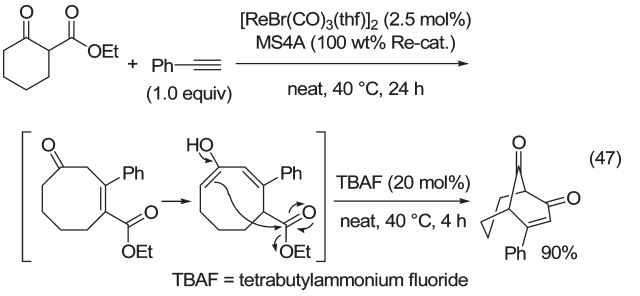
Kuninobu, Takai, and co-workers reported that a rhenium complex derived from $[ReBr(CO)_3(thf)]_2$ and isocyanide catalyzes the ring expansion reaction of cyclic β-keto esters (eq 46).[27,66] In this reaction, an alkyne inserts into a nonstrained C−C single bond of the β-keto ester. This reactivity is interesting because the nucleophilic addition of β-keto esters to terminal alkynes proceeds in the absence of isocyanide (vide infra).[26] By using the ring-expansion reaction, medium-sized cyclic compounds, which are usually difficult to construct, can be synthesized efficiently. The proposed reaction mechanism (Scheme 8) begins with the formation of a rhenacyclopentene intermediate by the reaction of a rhenium catalyst, β-keto ester, and terminal alkyne. There are two possible pathways from this point, with the difference being the timing of the reductive elimination step. Path A is a ring-opening by a *retro*-aldol reaction (2-a) followed by isomerization (3-a) and then reductive elimination (4-a). In path B, reductive elimination takes place first (2-b) followed by ring-opening via a *retro*-aldol reaction (3-b) and then isomerization (4-b).

Scheme 8. Proposed Mechanism for the Ring-Expansion Reactions

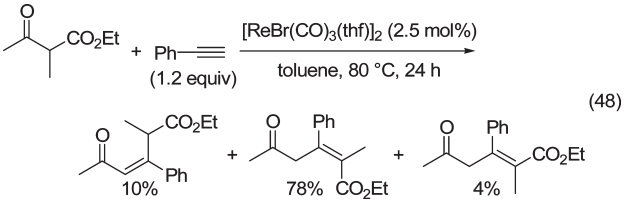




Such ring-expansion reactions can be applied to the synthesis of bicyclic compounds. When the reaction mixture shown in eq 46 is treated with tetrabutylammonium fluoride, bicyclo[3.3.1]nonene derivatives are formed in excellent yields (eq 47).[67] A proposed reaction mechanism for the formation of bicyclo[3.3.1]nonene derivatives from the corresponding eight-membered cyclic compounds[66] is as follows: (1) isomerization of the olefin moiety from the keto to the enol form and (2) intramolecular Claisen-type condensation via the elimination of ethanol.



The insertion of alkynes into C−C single bonds of cyclic β-keto esters also proceeds when acyclic β-keto esters are used as substrates (eq 48).[68]

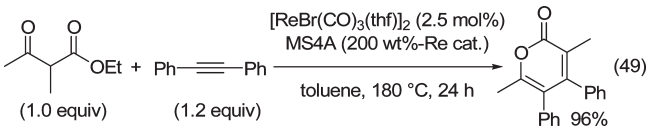


The combination of substrates and catalyst in this reaction is similar to that used for the insertion of terminal alkynes into the

dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

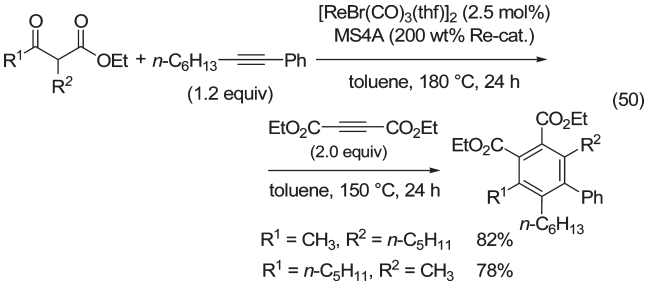
C−H bond of the active methylene group in β-keto esters (eq 15).[26] To clarify the reasons for the different reactivities, several experiments were conducted using an acyclic β-keto ester (eq 48). When the reaction between β-keto esters and phenylacetylene was carried out without any additive or solvent at 50 °C, the alkenylated β-keto esters shown in eq 15 were obtained as the major product. However, the selectivity for the products of eqs 15 and 48 changed dramatically when the reactions were conducted in toluene, at low concentrations, at higher temperatures, or with the addition of tetrahydrofuran (THF) or isocyanide.[69] On the basis of previous work, in which the authors reported that the dinuclear rhenium complex $[ReBr(CO)_3(thf)]_2$ is cleaved to a mononuclear rhenium complex $ReBr(CO)_3(thf)_2$ in THF,[70] Kuninobu and Takai assume that a dinuclear rhenium species promotes the production of the alkenylated β-keto ester, whereas the mixture of the products shown in eq 48 forms when the mononuclear species is present.

At higher temperatures than that used in eq 48, intramolecular cyclization via the elimination of an alcohol proceeds and 2-pyranone derivatives are produced in excellent yields (eq 49).[27,71]



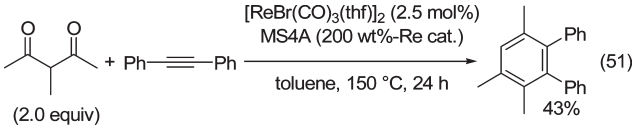
(49)

The 2-pyranones have subsequently been used for the regioselective synthesis of multisubstituted aromatic compounds through addition to the reaction mixture of a second alkyne that undergoes Diels−Alder cycloaddition (eq 50).[27,72] Using this method, regioisomers can be synthesized by changing the substituents R^1 and R^2 on the β-keto esters.



(50)

Another type of aromatization proceeds with 1,3-diketones and alkynes (eq 51).[73] From ^{13}C labeling experiments and the positions of the substituents in the substrates and products, it can be determined that the aromatic compounds are derived from 1,3-diketones, alkynes, and a portion of a second 1,3-diketone. This reaction is a rhenium-catalyzed formal [2 + 2 + 1 + 1]-cycloaddition between 1,3-diketones and alkynes.

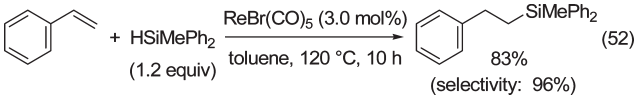


(51)

3. C−SI BOND FORMATION

Hydrosilylation of carbon−carbon double or triple bonds is one of the most direct and efficient methods for constructing carbon−silicon bonds. Therefore, there have been many reports on such transformations using transition metal complexes of platinum, rhodium, and ruthenium as catalysts.[74] In the addition of hydrosilanes to alkenes, electron-deficient hydrosilanes, such as $HSiR_nCl_{3-n}$ ($n = 0, 1$) and H_mSiR_{4-m} ($m = 2, 3$), have usually been used.[75] In contrast, the examples of hydrosilylation reactions of alkenes with hydrosilanes $HSiR^3$ (R^3 = alkyl, aryl) are relatively rare.[76]

Zhao and Hua reported that the rhenium complex $ReBr(CO)_5$ catalyzes the hydrosilylation of styrenes (eq 52).[77] In this reaction, the silyl group is regioselectively introduced at the terminal position of the olefin moiety in good to high yields. Notably, hydrosilylation proceeds even in the presence of a chlorine or bromine atom without reduction of the carbon−halogen bond of the styrenes.

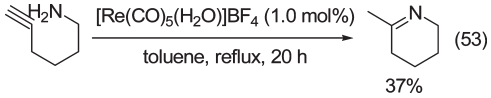


(52)

4. C−N BOND FORMATION

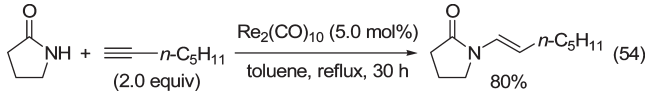
Hydroamination and hydroamidation of carbon−carbon double and triple bonds are efficient and useful transformations for the synthesis of amines, imines, and enamides.[78] However, it is usually difficult to control the regio- and setereoselectivity of the addition of amines or amides to alkynes.

Yan and co-workers reported that the rhenium complex $[Re(CO)_5(H_2O)]BF_4$ catalyzes the intramolecular hydroamination of alkynes (eq 53).[79] In this reaction, the hydroamination products are generated as the 5-exo and 6-exo forms. This reaction also proceeds with such soft Lewis acid catalysts as $[Cu(NCCH_3)_4]PF_6$, $Zn(OSO_2CF_3)_2$, and $[Pd(triphos)](OSO_2CF_3)_2$.



(53)

Intermolecular hydroamidation of unactivated terminal alkynes has also been reported (eq 54).[80] This reaction proceeds following the *anti*-Markovnikov rule, and only (*E*)-enamides are produced regio- and stereoselectively.

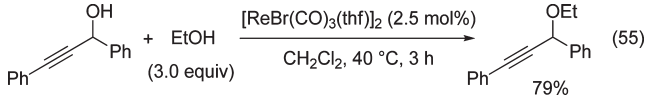


(54)

5. C−O BOND FORMATION

5.1. Nucleophilic Addition

The coupling of propargyl alcohols with several nucleophiles catalyzed by $[ReBr(CO)_3(thf)]_2$ has been revealed (eq 55).[23] Using alcohols as nucleophiles, carbon−oxygen bonds are constructed, providing the corresponding propargyl ethers.

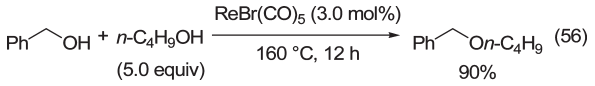


(55)

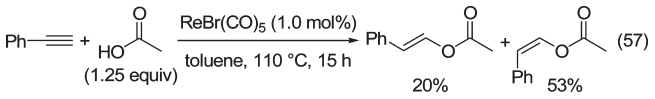
The rhenium complex $ReBr(CO)_5$ catalyzes the etherification of benzyl alcohols via dehydration (eq 56).[81] By using an excess amount of aliphatic alcohols in the presence of air, alkyl benzyl ethers are generated in high yields. It has been proposed that the

dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

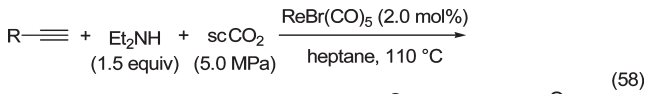
catalytic species is a rhenium(III)−oxo complex, which would be formed by the oxidation of $ReBr(CO)_5$.

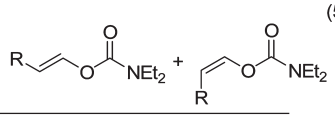


Hua and Tian reported that rhenium complex $ReBr(CO)_5$ catalyzes the addition of carboxylic acids to terminal alkynes (eq 57).[82] This reaction proceeds with high regioselectively to give *anti*-Markovnikov adducts. However, a mixture of *E*- and *Z*-isomers was obtained. Interestingly, the reaction predominantly affords the unusual *Z*-adduct.



The synthesis of alkenyl carbamates by coupling of terminal alkynes, Et_2NH, and CO_2 has also been achieved (eq 58).[83] In this reaction, *anti*-Markovnikov adducts are formed. The products are generated as mixtures of *E*- and *Z*-isomers; the *Z*-adduct, which is thermally unstable compared with the *E*-adduct, is however again formed as the main product.

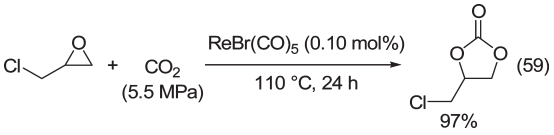




R =	Ph	24 h	8%	63%
	n-C_6H_{13}	35 h	47%	51%

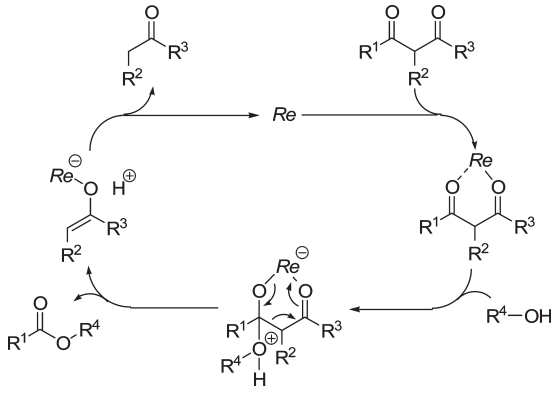
5.2. Esterification and its Retro Reaction

Catalytic transformations of CO_2 to produce useful organic compounds have received much attention as potential methods for solving environmental and industrial problems and providing new sources of raw materials. Lewis acids, including transition metal complexes that catalyze reactions between epoxides and CO_2, are well-known. Hua and co-workers reported that $ReBr(CO)_5$ also acts as a Lewis acid in the reaction between epoxides and supercritical CO_2 under solvent-free conditions to produce cyclic carbonates (eq 59).[84]

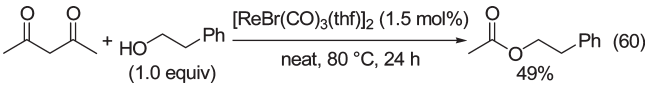


Kuninobu, Takai, and co-workers revealed that 1,3-diketones and alcohols react to produce esters (eq 60).[85] This reaction proceeds via carbon−carbon single-bond cleavage in a retro-aldol reaction. By using cyclic 1,3-diketones, the corresponding keto esters can be synthesized easily. The yields of esters are improved by using Lewis acids such as $In(OTf)_3$, $Fe(OTf)_3$, AgOTf, and $Cu(OTf)_2$ instead of the rhenium complex.[85,86] The proposed reaction mechanism is as follows (Scheme 9): (1) coordination of the cyclic 1,3-dicarbonyl compound to the rhenium center; (2) nucleophilic attack of the alcohol on a carbonyl group of the cyclic 1,3-dicarbonyl compound; (3) carbon−carbon bond cleavage via a retro-aldol-type reaction

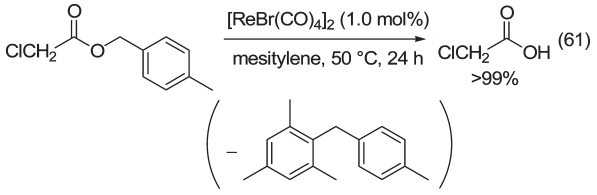
Scheme 9. Proposed Mechanism for the Formation of Esters via C−C Single-Bond Cleavage



(ring-opening reaction); and (4) quenching of the formed enolate by a proton to give the keto ester and regenerate the rhenium catalyst. In this mechanism, step (3) is important because it leads to the formation of esters and characterizes the reactivity of the reaction.

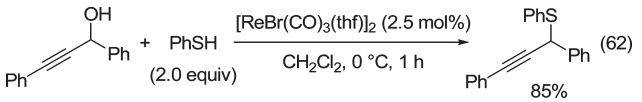


Benzyl esters are widely used as protecting groups for carboxylic acids. Lewis acids, such as $AlCl_3$, BCl_3, and BF_3, are commonly used as deprotecting reagents. In this deprotection reaction, at least 1 equiv of Lewis acid is required. In contrast, rhenium complexes, including $[ReBr(CO)_4]_2$, $ReBr(CO)_5$, and $ReCl(CO)_5$, have been shown to be useful catalysts for the deprotection of benzylic esters (eq 61).[87] Preston and co-workers concluded that *p*-$MeC_6H_4CH_2$ is a suitable protecting group with a working temperature of 50 °C. In this process, the Friedel−Crafts alkylation of aromatic compounds, which is described in eq 3, is used as a key reaction.[12]



6. C−S AND C−SE BOND FORMATION

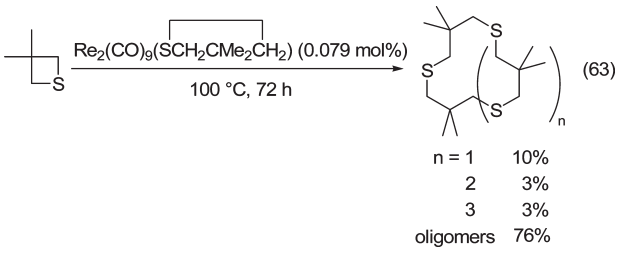
The coupling of a propargyl alcohol and thiophenol is catalyzed by $[ReBr(CO)_3(thf)]_2$ (eq 62).[23] In this reaction, a new carbon−sulfur bond is constructed, whereas a carbon−carbon bond is formed in the case of phenol.



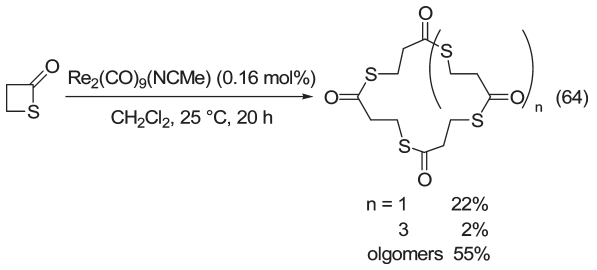
Polythiaether macrocycles have attracted interest because of their potential to serve as ligands.[88] Cyclooligomerization of thietane has been reported by Adams and co-workers (eq 63).[89] By using this method, polythiaether macrocycles are formed as a mixture of several cyclic oligomers. The reaction has been extended

dx.doi.org/10.1021/cr100241u |*Chem. Rev.* 2011, 111, 1938–1953

to macrocyclization of 3,3-dimethylselenatane.[90] Polyselenoether macrocycles also have good potential to serve as ligands,[91] but examples of known polyselenoether macrocycles are rare.[92]

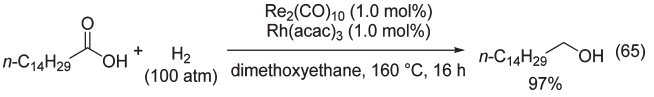


Adams and McBride also reported that a similar reaction proceeds using β-propiothiolactone (eq 64).[93]

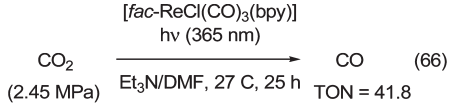


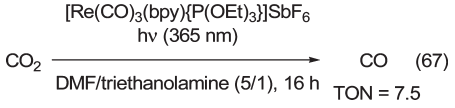
7. REDUCTION

Transition-metal-catalyzed hydrogenation of carbonyl compounds has served as one of the most useful tools for the transformation of functional groups. McAlees and McCrindle established the following increasing order of substrate difficulty for such reactions: acid chlorides > aldehydes, ketones > anhydrides > esters > carboxylic acids > amides.[94] Fuchikami and co-workers reported the reduction of carboxylic acids to alcohols by dihydrogen (eq 65).[95] In this reaction, a bimetallic catalyst, a combination of $Re_2(CO)_{10}$ and $Rh(acac)_3$, is effective for promoting efficient reduction. The yield of the alcohol is very low (1−2%) when only $Re_2(CO)_{10}$ or $Rh(acac)_3$ is used as the catalyst. Interestingly, this reaction has unique selectivity for reduction of the carboxylic acid moiety rather than the ester functionality.



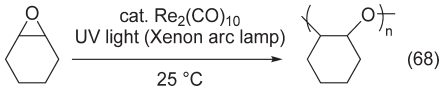
Reduction of CO_2 has received much attention because CO_2 has the possibility of being used as a carbon source. It has been well-known that rhenium complexes $ReX(CO)_3(bpy)$ (X = Cl, Br; bpy = 2,2-bipyridine) can act as photocatalysts for the reduction of CO_2 to CO (eq 66).[96] Therefore, several groups have reported on this reduction by modifying the structure of the rhenium catalysts (eq 67).[97,98]





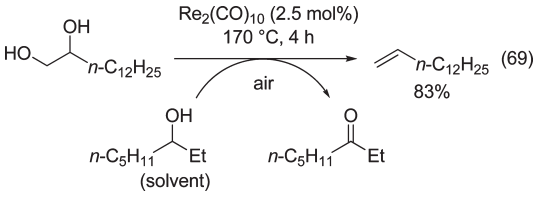
8. POLYMERIZATION

The rhenium complex $Re_2(CO)_{10}$ initiated the polymerization of cyclohexene oxide photochemically at 25 °C (eq 68).[99] This reaction did not require any cocatalyst. However, Abu-Abdoun found that the polymerization proceeds very slowly. He suggested that the polymerization occurs after activation of cyclohexene oxide by the unsaturated rhenium species $[Re(CO)_4]_2$, which is formed by the irradiation of UV light. Pentacarbonylrhenium(I) halides $ReX(CO)_5$ (X = Cl, Br, I) also show catalytic activity for the polymerization of cyclohexene oxide.[100] The rate of polymerization is faster for X = Cl than it is for X = Br or I.



9. MISCELLANEOUS

Areceo, Ellman, and Bergman reported didehydroxylation of vicinal diols to alkenes (eq 69).[101] In this reaction, a simple alcohol works as a reducing agent. By using this reaction, both terminal and internal vicinal diols are deoxygenated to olefins without isomerization of the olefin moiety. Although the authors indicated that the mechanism of this reaction is still unknown, they proposed that oxidized rhenium species might be the active catalyst because this reaction did not proceed in the absence of O_2. The authors also hypothesized the formation of a rhenium diolate species.



10. CONCLUSION

As described in the above sections, many types of reactions have recently been discovered using rhenium carbonyl complexes as catalysts. Prior to 2000, rhenium carbonyl complexes were used as hard Lewis acid catalysts to promote C−C bondformation reactions, including Friedel−Crafts reactions, Mukaiyama aldol reactions, and Knoevenagel reactions. It is interesting that some reactions proceed even in the presence of a small amount of water. In addition, C−O, C−S, and C−Se bond-forming reactions and reduction of carboxylic acids and CO_2 have also been reported. Since about 2000, rhenium carbonyl complexes have also been employed as soft Lewis acids. By using this reactivity, cyclization reactions and nucleophilic additions of carbon nucleophiles to alkynes or allenes have been achieved via the activation of the unsaturated substrates by the rhenium catalyst or the formation of rhenacyclic intermediates. C−Si, C−N, and C−O bonds have also been constructed using rhenium carbonyl catalysts. In almost all of these cases, similar reactions were previously known to be promoted by other transition metal complexes. Since 2005, rhenium carbonyl catalyzed transformations via C−H and C−C bond cleavage, which are the key reactions for highly efficient transformations, have been realized. In these examples, it is noteworthy that typical

rhenium carbonyl catalyzed reactions are effective. At present, it is clear that rhenium carbonyl complexes have a variety of catalytic activities. In the future, it is expected that more information about the reactivities of rhenium carbonyl complexes will be clarified, and additional novel as well as more typical reactions catalyzed by rhenium carbonyl complexes will be discovered.

AUTHOR INFORMATION

Corresponding Author

*E-mail:kuninobu@cc.okayama-u.ac.jp; ktakai@cc.okayama-u.ac.jp.

BIOGRAPHY

Yoichiro Kuninobu is an Assistant Professor at Okayama University in Japan. He was born in Japan (Kanagawa) in 1976. He received his B.S. and Ph.D. degrees from the University of Tokyo in 1999 and 2004, respectively, under the supervision of Professor Eiichi Nakamura. He was appointed to his current position of an Assistant Professor at Okayama University in 2003 and is now working with Professor Kazuhiko Takai. He has been recognized with the following awards: Meiji Seika Award in Synthetic Organic Chemistry, Japan (2006), BCSJ Award (2008), and Banyu Chemist Award (BCA 2010). His research interests are related to the development of novel and highly efficient synthetic organic reactions using transition metal catalysts.

Kazuhiko Takai was born in Tokyo, Japan, in 1954. He received his B.E. and Ph.D degrees from Kyoto University under the direction of Professor Hitosi Nozaki. In 1981, he was appointed as an assistant professor of Prof. Nozaki's group at Kyoto University. During that time he joined Prof. Clayton H. Heathcock's group at the University of California, Berkeley, as a postdoctoral fellow (1983−1984). In 1994, he moved to Okayama University as an associate professor, and became a full professor in 1998. He received the Chemical Society of Japan Award for Young Chemists (1989) and Synthetic Organic Chemistry Award, Japan (2008). He has developed several synthetic methods using early transition metals such as chromium and titanium. Current research in his group is aimed towards the use of the complexes of group 7 metals as catalysts in organic synthesis.

ACKNOWLEDGMENT

This work was partially supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

REFERENCES

(1) (a) Boag, N. M.; Kaesz, H. D. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, pp 161−242. (b) O'Connor, J. M. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 6, pp 167−229. (c) Hoffman, D. M. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 6, pp 231−255. (d) Romão, C. C.; Royo, B. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, the Netherlands, 2007; Vol. 5, pp 855−960.

(2) (a) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149. (b) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169. (c) Espenson, J. H. *Adv. Inorg. Chem.* 2003, *54*, 157.(d) Kühn, F. E.; Santos, A. M.; Herrmann, W. A. *Dalton Trans.* **2005**, 2483.

(3) There have been a few reviews of rhenium-catalyzed transformations. See: (a) Kusama, H.; Narasaka, K. *J. Synth. Org. Chem. Jpn.* **1996**, *54*, 644. (b) Hua, R.; Jiang, J.-L. *Curr. Org. Synth.* **2007**, *4*, 151.

(4) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277.

(5) Ingham, W. L.; Coville, N. J. *J. Organomet. Chem.* **1992**, *423*, 51.

(6) (a) Harris, G. W.; Coville, N. J. *Organometallics* **1985**, *4*, 908. (b) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* 1985, *4*, 914.

(7) (a) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933. (b) Kaesz, H. D. *J. Organomet. Chem.* **1980**, *200*, 145.

(8) (a) George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977. (b) Rossenaar, B. D.; Stufkens, D. J.; Vlček, A., Jr. *Inorg. Chem.* **1996**, *35*, 2902.

(9) Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391.

(10) Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2005**, *127*, 13498.

(11) Kusama, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2379.

(12) Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2779.

(13) Hua, R.; He, J.; Sun, H. *Chin. J. Chem.* **2007**, *25*, 132.

(14) Kuninobu, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2009**, *131*, 9914.

(15) Hirano, M.; Hirai, M.; Ito, Y.; Tsurumaki, T.; Baba, A.; Fukuoka, A.; Komiya, S. *J. Organomet. Chem.* **1998**, *569*, 3.

(16) Zuo, W.-X.; Hua, R.; Qiu, X. *Synth. Commun.* **2004**, *34*, 3219.

(17) Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Tetrahedron Lett.* **2005**, *46*, 787.

(18) Nishiyama, Y.; Shimoura, K.; Sonoda, N. *Tetrahedron Lett.* **2008**, *49*, 6533.

(19) Nishiyama, Y.; Kaiba, K.; Umeda, R. *Tetrahedron Lett.* **2010**, *51*, 793.
(20) Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3296.
(21) Kuninobu, Y.; Inoue, Y.; Takai, K. *Chem. Lett.* **2006**, *35*, 1376.
(22) Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319.
(23) Kuninobu, Y.; Ueda, H.; Takai, K. *Chem. Lett.* **2008**, *37*, 878.
(24) Bolm, C.; Kesselgruber, M.; Hermanns, N.; Hildebrand, J. P.; Raabe, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1488.
(25) Nakamura, M.; Endo, K.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13002.
(26) Kuninobu, Y.; Kawata, A.; Takai, K. *Org. Lett.* **2005**, *7*, 4823.
(27) Kuninobu, Y.; Kawata, A.; Yudha, S. S.; Takata, H.; Nishi, M.; Takai, K. *Pure Appl. Chem.* **2010**, *82*, 1491.
(28) (a) Kennedy-Smith, J. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4526. (b) Ochida, A.; Ito, H.; Sawamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 16486.
(29) Gao, Q.; Zheng, B.-F.; Li, J.-H.; Yang, D. *Org. Lett.* **2005**, *7*, 2185.
(30) Deng, C.-L.; Zou, T.; Wang, Z.-Q.; Song, R.-J.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 412.
(31) Deng, C.-L.; Song, R.-J.; Liu, Y.-L.; Li, J.-H. *Adv. Synth. Catal.* **2009**, *351*, 3096.
(32) Kuninobu, Y.; Yamashita, A.; Yamamoto, S.-i.; Yudha, S. S.; Takai, K. *Synlett* **2009**, 3027.
(33) Zhao, W.-G.; Hua, R. *Tetrahedron* **2007**, *63*, 11803.
(34) Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 468.
(35) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928.
(36) Saito, K.; Onizawa, Y.; Kusama, H.; Iwasawa, N. *Chem.—Eur. J.* **2010**, *16*, 4716.
(37) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104.
(38) Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289.
(39) Kuninobu, Y.; Yu, P.; Takai, K. *Chem. Lett.* **2007**, *36*, 1162.
(40) Yudha, S. S.; Kuninobu, Y.; Takai, K. *Angew. Chem., Int. Ed.* 2008, *47*, 9318.
(41) Kuninobu, Y.; Nishi, M.; Yudha, S. S.; Takai, K. *Org. Lett.* **2008**, *10*, 3009.
(42) Tsuji, H.; Yamagata, K.-i.; Fujimoto, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 7792.
(43) Yoshikai, N.; Zhang, S.; Yamagata, K.-i.; Tsuji, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 4099.
(44) Kuninobu, Y.; Iwanaga, T.; Nishi, M.; Takai, K. *Chem. Lett.* **2010**, *39*, 894.
(45) Kawata, A.; Kuninobu, Y.; Takai, K. *Chem. Lett.* **2009**, *38*, 836.
(46) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1988**, *29*, 3833.
(47) Hori, H.; Koike, K.; Takeuchi, K.; Ishitani, O. *Chem. Lett.* **2000**, *29*, 376.
(48) Farona, M. F.; Greenlee, W. S. *J. Chem. Soc., Chem. Commun.* **1975**, 759.
(49) For examples, see: (a) Ohmura, T.; Yorozuya, S.-i.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2000**, *19*, 365. (b) Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 11107. (c) Ogoshi, S.; Ueta, M.; Oka, M.-a.; Kurosawa, H. *Chem. Commun.* **2004**, 2732. (d) Lee, C.-C.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. *Organometallics* **2005**, *24*, 136. (e) Chen, X.; Xue, P.; Sung, H. H. Y.; Williams, I. D.; Peruzzini, M.; Bianchini, C.; Jia, G. *Organometallics* **2005**, *24*, 4330. (f) Weng, W.; Guo, C.; Çelenligil-Çetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197. (g) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2007**, *349*, 933. (h) Ogata, K.; Oka, O.; Toyota, A.; Suzuki, N.; Fukuzawa, S.-i. *Synlett* **2008**, 2663.
(50) (a) Kakiuchi, F.; Murai, S. *Top. Organomet. Chem.* **1999**, *3*, 47. (b) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (c) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (d) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013.
(51) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211.
(52) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.
(53) Kuninobu, Y.; Nishina, Y.; Okaguchi, K.; Shouho, M.; Takai, K. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1393.
(54) Kuninobu, Y.; Nishina, Y.; Shouho, M.; Takai, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2766.
(55) Kuninobu, Y.; Nishina, Y.; Takai, K. *Org. Lett.* **2006**, *8*, 2891.
(56) Kuninobu, Y.; Nishina, Y.; Kawata, A.; Shouho, M.; Takai, K. *Pure Appl. Chem.* **2008**, *80*, 1149.
(57) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 202.
(58) Kuninobu, Y.; Nishina, Y.; Nakagawa, C.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 12376.
(59) Kuninobu, Y.; Nishina, Y.; Takai, K. *Tetrahedron* **2007**, *63*, 8463.
(60) Kuninobu, Y.; Matsuki, T.; Takai, K. *Org. Lett.* **2010**, *12*, 2948.
(61) (a) Kuninobu, Y.; Tokunaga, Y.; Takai, K. *Chem. Lett.* **2007**, *36*, 872. (b) Kuninobu, Y.; Kikuchi, K.; Tokunaga, Y.; Nishina, Y.; Takai, K. *Tetrahedron* **2008**, *64*, 5974.
(62) Kuninobu, Y.; Fujii, Y.; Matsuki, T.; Nishina, Y.; Takai, K. *Org. Lett.* **2009**, *11*, 2711.
(63) Kuninobu, Y.; Nishina, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2008**, *130*, 14062.
(64) Kuninobu, Y.; Yu, P.; Takai, K. *Org. Lett.* **2010**, *12*, 4274.
(65) Zhang, Y. J.; Skucas, E.; Krische, M. J. *Org. Lett.* **2009**, *11*, 4248.
(66) Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 11368.
(67) Kuninobu, Y.; Morita, J.; Nishi, M.; Kawata, A.; Takai, K. *Org. Lett.* **2009**, *11*, 2535.
(68) Kuninobu, Y.; Kawata, A.; Nishi, M.; Yudha, S. S.; Chen, J.-j.; Takai, K. *Chem. Asian J.* **2009**, *4*, 1424.
(69) : Suginome, M.; Ito, Y. (Ed.: Murai, S.) *Top. Organomet. Chem.* **1999**, *3*, 131.
(70) Vitali, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1972**, *102*, 587.
(71) Kuninobu, Y.; Kawata, A.; Nishi, M.; Takata, H.; Takai, K. *Chem. Commun.* **2008**, 6360.
(72) Kuninobu, Y.; Takata, H.; Kawata, A.; Takai, K. *Org. Lett.* **2008**, *10*, 3133.
(73) Kuninobu, Y.; Nishi, M.; Kawata, A.; Takata, H.; Hanatani, Y.; Yudha, S. S.; Iwai, A.; Takai, K. *J. Org. Chem.* **2010**, *75*, 334.
(74) Yamamoto, K.; Hayashi, T. *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 167−191.
(75) (a) Hayashi, T. *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 1, pp 319−333. (b) Yamamoto, K.; Hayashi, T. *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 167−181.(c) Pedersen, H. L.; Johannsen, M. *J. Org. Chem.* **2002**, *67*, 7982. (d) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640. (e) Horino, Y.; Livinghouse, T. *Organometallics* **2004**, *23*, 12.
(76) (a) Lewis, L. N.; Sy, K. G.; Bryant Jr, G. L.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750. (b) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098. (c) Giraud, L.; Jenny, T. *Organometallics* **1998**, *17*, 4267. (d) Chatani, N.; Kodama, T.; Kajikawa, Y.; Murakami, H.; Kakiuchi, F.; Ikeda, S.-i.; Murai, S. *Chem. Lett.* **2000**, *29*, 14. (e) Yamamoto, Y.; Ohno, T.; Itoh, K. *Organometallics* **2003**, *22*, 2267. (f) Itami, K.; Mitsudo, K.; Nishino, A.; Yoshida, J.-i. *J. Org. Chem.* **2002**, *67*, 2645. (g) Sprengers, J. W.; De Greef, M.; Duin, M. A.; Elsevier, C. J. *Eur. J. Inorg. Chem.* **2003**, 3811.
(77) Zhao, W.-G.; Hua, R. *Eur. J. Org. Chem.* **2006**, 5495.
(78) (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (c) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708. (d) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.
(79) (a) Müller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y. K. *Organometallics* **2000**, *19*, 170. (b) Ouh, L. L.; Müller, T. E.; Yan, Y. K. *J. Organomet. Chem.* **2005**, *690*, 3774.

(80) Yudha, S. S.; Kuninobu, Y.; Takai, K. *Org. Lett.* **2007**, *9*, 5609.
(81) Liu, Y.; Hua, R.; Sun, H.-B.; Qiu, X. *Organometallics* **2005**, *24*, 2819.
(82) Hua, R.; Tian, X. *J. Org. Chem.* **2004**, *69*, 5782.
(83) Jiang, J.-L.; Hua, R. *Tetrahedron Lett.* **2006**, *47*, 953.
(84) Jiang, J.-L.; Gao, F.; Hua, R.; Qiu, Q. *J. Org. Chem.* **2005**, *70*, 381.
(85) Kawata, A.; Takata, K.; Kuninobu, Y.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7793.
(86) Kuninobu, Y.; Kawata, A.; Noborio, T.; Yamamoto, S.-i.; Matsuki, T.; Takata, K.; Takai, K. *Chem. Asian J.* **2010**, *5*, 941.
(87) Davies, T. J.; Jones, R. V. H.; Lindsell, W. E.; Miln, C.; Preston, P. N. *Tetrahedron Lett.* **2002**, *43*, 487.
(88) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.
(89) (a) Adams, R. D.; Falloon, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 10540. (b) Adams, R. D.; Falloon, S. B. *Organometallics* **1995**, *14*, 1748. (c) Adams, R. D.; Queisser, J. A.; Yamamoto, J. H. *Organometallics* 1996, *15*, 2489.(d) Adams, R. D.; Perrin, J. L.; Queisser, J. A.; Wolfe, J. B. *Organometallics* **1997**, *16*, 2612.
(90) (a) Adams, R. D.; Huang, M.; Huang, W.; Queisser, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 9442. (b) Adams, R. D.; Huang, M.; Huang, W. *Organometallics* **1997**, *16*, 4479.
(91) (a) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Pinto, B. M.; Zhou, X.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3706. (b) Levason, W.; Quirk, J. J.; Reid, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3713.
(92) Hope, E. G.; Levason, W. *Coord. Chem. Rev.* **1993**, *122*, 109.
(93) (a) Adams, R. D.; McBride, K. T. *Chem. Commun.* **1997**, 525. (b) Adams, R. D.; McBride, K. T. *Organometallics* **1997**, *16*, 3895.
(94) McAlees, A. J.; McCrindle, R. *J. Chem. Soc., C* **1969**, 2425.
(95) He, D.-H.; Wakasa, N.; Fuchikami, T. *Tetrahedron Lett.* 1995, *36*, 1059.
(96) (a) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (c) Hori, H.; Takano, Y.; Koike, K.; Sasaki, Y. *Inorg. Chem. Commun.* **2003**, *6*, 300.
(97) For a review, see: Takeda, H.; Ishitani, O. *Coord. Chem. Rev.* **2010**, *254*, 346.
(98) (a) Ruiz, G.; Wolcan, E.; Capparelli, A. L.; Féliz, M. R. *J. Photochem. Photobiol. A: Chem.* **1995**, *89*, 61. (b) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *J. Photochem. Photobiol., A* **1996**, *96*, 171. (c) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. *Organometallics* **1996**, *15*, 3374. (d) Hori, H.; Johnson, F. P. A.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Chem. Soc., Dalton Trans.* **1997**, 1019. (e) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Kanno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724. (f) Hori, H.; Ishihara, J.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Photochem. Photobiol., A* **1999**, *120*, 119. (g) Hori, H.; Koike, K.; Takeuchi, K.; Sasaki, Y. *Chem. Lett.* **2000**, 522. (h) Sung-Suh, H. M.; Kim, D. S.; Lee, C. W.; Park, S.-E. *Appl. Organomet. Chem.* **2000**, *14*, 826. (i) Hwang, J.-S.; Kim, D. S.; Lee, C. W.; Park, S.-E. *Korean J. Chem. Eng.* **2001**, *18*, 919. (j) Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **2003**, *125*, 11976. (k) Kurz, P.; Probst, B.; Spingler, B.; Alberto, R. *Eur. J. Inorg. Chem.* **2006**, 2966. (l) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. *J. Am. Chem. Soc.* **2008**, *130*, 2023.
(99) Abu-Abdoun, I. I. *Polym. Int.* **1999**, *48*, 1197.
(100) Abu-Abdoun, I. I. *Des. Monomers Polym.* **2000**, *3*, 171.
(101) Arceo, E.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2010**, *132*, 11408.